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Interaction of Supercritical Carbon Dioxide with Polymers.

I. Crystalline Polymers

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SYNOPSIS

Supercritical fluid (SCF) technology involving carbon dioxide is recently receiving wide attention due to its vast potential application in various fields such as cleaning, extraction, synthesis, etc., in addition to its environmental benefits. To fully exploit the use of SCFs in new technologies, it is important to understand how SCFs interact with materials. To this end, we have undertaken a systematic study involving a wide pressure and temperature range to investigate the interaction of supercritical carbon dioxide (SC CO₂) with nine different crystalline polymers, namely, substituted and unsubstituted polyethylene (four varieties), polypropylene, nylon 66, poly(ethylene terephthalate), poly(oxymethylene), and poly(vinylidene fluoride). Critical factors such as changes in appearance and weight, temperature, pressure and time of the supercritical fluid treatment, and dimension of samples have been observed. The influence of SC CO₂ on the thermal properties of treated polymers has been investigated through TGA analysis. Further, changes in the mechanical properties such as yield strength, ultimate elongation, and modulus of elasticity of the investigated crystalline polymers were also observed. A discussion has been included to show the possible implications of the observed changes in realizing various applications. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Supercritical fluid (SCF) technology has been widely used in extraction and purification processes in the food and pharmaceuticals industry^{1,3} and for techniques such as supercritical fluid chromatography.⁴⁻⁶ Recently, there has been a significant increase in interest of the use of sub- as well as supercritical carbon dioxide (SC CO₂) as a substitute for chlorofluorocarbons (CFCs) for specific and specialized applications such as precision cleaning,⁷⁻⁹ in which the choices of environmentally acceptable alternatives are quite limited. Though many recent reports detail information about using SC CO₂ for various

applications, specific issues such as interaction with polymers, modification of surfaces of the treated polymers, changes in the mechanical properties, weight changes in the polymers, etc., have not been completely addressed.

In general, one can expect that most metal and glass substrates will have little interaction with carbon dioxide because of their high crystallinities and their general imperviousness to gases. Polymeric materials, on the other hand, may be expected to show a wide range of interactions with a supercritical fluid (or dense gas), varying from essentially no effect to very pronounced effects based upon dissolution or even degradation (chemical) of them.¹⁰ Consideration of the use of SCF as a cleaning agent in conjunction with polymeric materials requires a thorough knowledge of the interaction of polymers with super- and subcritical carbon dioxide. Depending on the observed effects (either no effect or even detrimental effect), one can visualize a wide choice

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of applications such as extraction, precision cleaning, or depolymerization.

SC CO₂

SC CO₂ has a critical temperature of 31.06° C and a critical pressure of 1070 psi (73.8 atm). Carbon dioxide offers a number of advantages including low human toxicity, general chemical inertness, non-combustibility, natural occurrence, low cost, ready availability, complete recovery of the extracting agent and extracted substances, environmental acceptability (no ozone depletion), and solubility characteristics similar to organic solvents like chlorofluorocarbons (CFCs). Owing to CFCs implication in ozone depletion, their eventual replacement in industrial and commercial needs has recently become one of primary concerns.^{8,11}

SC CO₂ is also attractive from a waste minimization view point. After the cleaning step, non-hazardous carbon dioxide is separated from the contaminants, leaving only the contaminant waste stream and pure, recyclable CO₂. Because super- and subcritical carbon dioxide have many similarities to CFCs such as solubility, it is one of the ideal candidates to replace them. Further, the comparable viscosity and extraction capability of the supercritical phase with respect to gas and liquid, respectively, are quite noticeable factors. Thus, SCFs possess the cleaning ability to penetrate even under very small cavities, such as beneath the package of surface-mounted electronic components. Moreover, issues such as surface tension (while considering the "wettability" of cleaning agents with the surface to be cleaned) is not a matter of concern because SCFs (dense gases) are perfectly wetting.

In this context, one has to take into account the absorption of gases and vapors. The absorption of CO₂ in polymers can plasticize the material and, in turn, decrease the glass transition temperature. Further, it can also induce crystallization of the material and cause an increase in the melting temperature and melting enthalpy. At sufficiently high pressures, the absorption of certain gases can result in substantial swelling of the polymer upon the release of pressure, which can be beneficial or deleterious. Swelling of a solid polymer matrix with a high pressure gas can, however, aid in the deposition of temperature-sensitive materials into the polymer. It has been shown^{12,13} that substances such as fragrances, pest-control agents, and pharmaceutical drugs can be impreg-

nated in a solid polymer by exposing the polymer to SCF.

Swelling of the polymer by SCF effectively increases the diffusion coefficient of the heavy dopant by several orders of magnitude; this allows it to migrate into the polymer matrix within a reasonable time. When the system is depressurized, the dissolved gas readily diffuses from the polymer; while the heavy dopant, which is trapped in the matrix, slowly diffuses out of the solid at a rate now orders of magnitude slower than the rate it was put into the polymer. This technique can be used to form novel controlled-release devices, because very large molecules can be impregnated into a swollen polymer matrix at operating temperatures low enough to avoid thermal degradation of materials. In addition, applications such as separation of thermoplastics from each other as well as from contaminants by treating with pure CO₂ and a mixture of CO₂-SF₆ have been realized^{14,15} for their recycling and to improve the properties of the reprocessed materials.

The potential interactions between a polymeric material and SC CO₂, and possible applications are outlined schematically in Figure 1. The plasticization and crystallization in polymers due to the absorption of CO₂ will decrease the glass transition temperature and increase the melting temperature and melting enthalpy. Further, one can also expect changes in mechanical and surface properties of polymers. In this article we will address the changes in the physical, thermal, and mechanical properties of crystalline polymers due to the interaction with SC CO₂. In this regard, it is worth mentioning about the earlier reported works involving silicone rubber, polycarbonate,¹⁶ cellulose acetate,¹⁷ poly(vinylidene fluoride), poly(methyl methacrylate),¹⁸ polystyrene,¹⁹ and poly(ethylene terephthalate).²⁰ Most of the earlier reported works address one specific phenomenon such as plasticization or dilation, low temperature melting behavior, or solubility of carbon dioxide, and did not make any correlation or describe the overall effect. Further, the phenomenon of absorption and swelling have not been studied on a broad spectrum of polymers under conditions that approximate reasonable processing conditions for materials that may be used in manufacturing. So we have treated a series of crystalline polymers in both sub- and supercritical carbon dioxide under seven different experimental conditions. These results will be discussed in general to isolate important factors that affect the weight change (and possibly the dimensions) of polymers.

EXPERIMENTAL

Materials

Nine different polymers (listed in Table I) of crystalline nature have been employed to investigate the interaction of supercritical carbon dioxide and evaluate the impact on different parameters. All of them are from commercially available sources in sheets of varying thicknesses ranging from 0.80–3.20 mm. The carbon dioxide gas used in all experiments is pure grade (Grade 2.8, Bone dry) from US Airgas, Inc.

Methods

Preparation of Polymer Samples

From the commercially available polymers, samples of 1 × 4 cm sizes were cut out using a guide mold, to have uniform surface area for all the samples.

Supercritical Carbon Dioxide Treatment and Testing Procedures

The treatments were performed in a system comprised of a 5-L, high-pressure windowless reactor and a 1-L windowed separator vessel (a high-pres-

Table I Employed Polymers

Polymer ID	Polymer	Commercial Name
HDPE	High-density polyethylene	
HMWPE	High-molecular weight Polyethylene	
LDPE	Low-density polyethylene	
Nylon 66	Nylon 66	Nylon 66
PET	Poly(ethylene terephthalate)	Mylar
POM	Poly(oxymethylene)	Delrin
PP	Polypropylene	
PVDF	Polyvinylidene fluoride	Kynar
Teflon	Polytetrafluoroethylene	Teflon

sure optical cell with a sapphire window). The experimental configuration is depicted in a flow chart (Fig. 2). The samples were uniformly distributed in the high-pressure stainless steel reactor equipped with an air-driven mechanical stirrer, which mixes the SCF at a steady rate, allowing a uniform exposure of the samples. The carbon dioxide gas has been injected to the reactor through a high-pressure pump (HP), after passing through a gas filter (F). All the units (which are holding high pressures) are adapted with rupture discs (RD) for safety considerations.

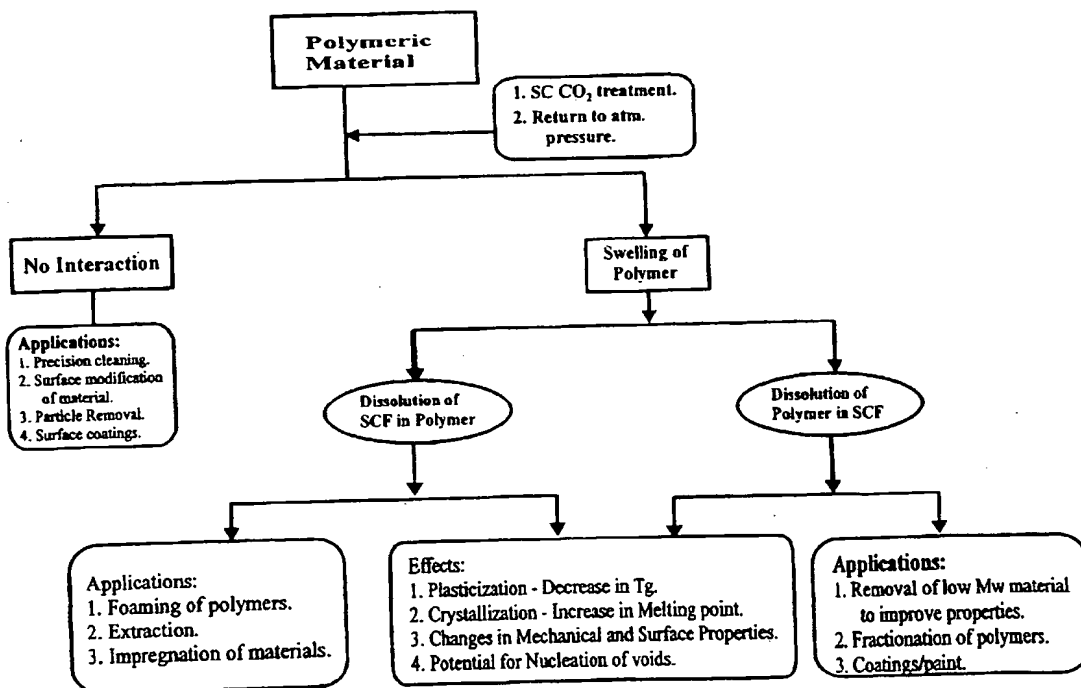


Figure 1 Flow diagram of the interaction of carbon dioxide with polymers.

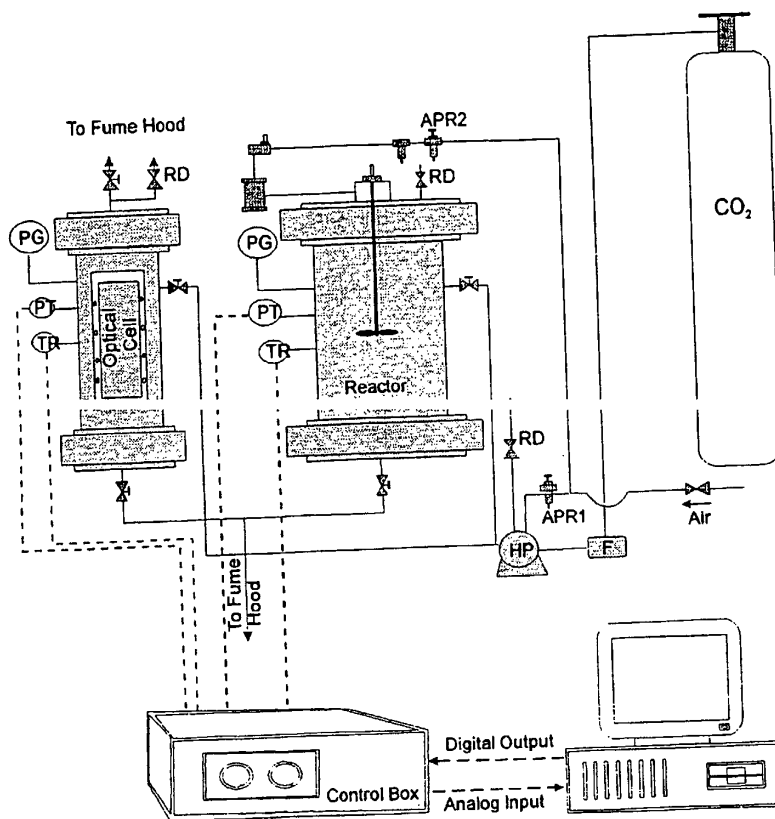


Figure 2 Schematic diagram of supercritical carbon dioxide treatment system. F = filter; HP = high-pressure pump; RD = rupture disc; PG = pressure gauge; PT = pressure transducer; TR = temperature readout; APR1 and APR2 = air-pressure regulators.

The pressure transducer (PT) and temperature readout (TR) from the reactor and separator vessels were connected through a control box to a computer, to monitor the pressure and temperature in real time. The pressure-gauge (PG) attached to both the vessels can also be manually read to note the pressure.

In all the experiments, both the treatment time and decompression time were fixed as 1 h, except one in which 5-h decompression time was applied. The experimental conditions are listed in Table II. Note that the decompression time is the time over which the pressure was released from the treatment vessel. Each experiment has been performed with five identical samples and, hence, the reported data is an average of five values, with a standard deviation of < 2%. After treatment, the effect of SCF treatment was monitored gravimetrically (by taking the weights up to ten thousandth of a gram) at seven different time intervals. The samples were always

stored in cleaned, dust-free polyethylene bags at room temperature ($23 \pm 2^\circ\text{C}$).

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) evaluations were performed using a Perkin-Elmer DSC-2C to obtain the T_g , T_m , and DH. A Du Pont Model 2950 TGA was used to evaluate the total amount of carbon dioxide uptake in polymers. A constant heating rate of $20^\circ\text{C}/\text{min}$ was used in both the DSC and TGA evaluations.

RESULTS AND DISCUSSION

A systematic supercritical carbon dioxide treatment involving wide pressure range from 1000–3000 psi and temperature from 25 to 70°C with nine different commercially available polymers has been performed. The changes in physical, thermal, and mechanical properties due to the treatment have been

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Table II Carbon Dioxide Conditions Employed in Polymer Treatments

Condition	Pressure (psi)	Temperature (°C)	Exposure Time (h)	Decompression Time (h)	CO ₂ Phase
C (Control)	14.7	25	—	—	—
C1	1000	25	1	1	Liquid
C2	1000	40	1	1	Gas
C3	2000	40	1	1	SCF
C4	3000	25	1	1	Liquid
C5	3000	40	1	1	SCF
C6	3000	70	1	1	SCF
C7	3000	70	1	5	SCF

monitored to evaluate the interactions and effects on these polymers.

Changes in Appearance

In any consideration for the substitution of SCF technology for CFCs in cleaning requires a careful attention to many factors that may be affected in the cleaning operation, such as the appearance of the material. In cleaning applications, it is important that there are no visual changes in materials; however, in other applications such as disassembly or separation of materials for eventual recycling (or reuse), it will not play any role at all.²¹ Though no major distortive effect or no gross deformation was observed in most of the samples under the treatment conditions listed in Table II, in some of the samples bubbles appeared after decompression. Among the investigated polymers, except LDPE and PP, no significant change in appearance was noticed under the treatment conditions C1–C7. In LDPE, though no change was noted up to the pressure range 1000 psi (treatment conditions C1 and C2), some bubbles appeared after treatment at 3000 psi (C5–C7). Figures 3 and 4 show the post-CO₂-treated samples of LDPE. In the case of Polypropylene, samples turned to a light yellow color from its initial colorless state. The evolution of color suggests the formation of scattering domains (bubbles) leading to Rayleigh/Mie (particle)-type scattering (note that the bubble dimensions may roughly be on the order of the wavelength of visible light or smaller).

In this context, one should note the effect of decompression time, which was evaluated at two different points: (1) a 1-h decompression and (b) a 5-h decompression. Not surprisingly, the longer decompression times showed the least effect on any polymer that showed significant carbon dioxide uptake. Thus, samples that were decompressed over 5 h showed significantly less or no effect. The picture

(Fig. 4) also shows how dramatic such changes may be. The practical aspects of these studies suggest that the use of high pressures and short decompression times would be, without question, inappropriate for the cleaning of materials containing polymers prone to the absorption of large amounts of carbon dioxide (such as acrylates).²²

Weight Changes of Polymers

The polymers were treated under the conditions noted in Table II, and weight change of the polymers was monitored gravimetrically. We have evaluated gravimetric changes for the investigated polymers at three different pressures, namely 1000, 2000, and 3000 psi at 40°C (Table II). Further, the effect of temperature was also monitored by carrying out experiments from 25 to 70°C at a constant pressure of 3000 psi. The absorption/dissolution of carbon dioxide into a material is readily noted either (1) by observing a large positive change in the weight of the sample proportional to factors such as total surface area and surface to volume ratios, or (2) by the presence of extensive foam or bubble formation in the sample. These effects indicate that the treated polymer is significantly plasticized by the carbon dioxide. This effect will be further discussed under thermal properties.

The fundamental mechanisms that contribute to the observed changes are: (a) the carbon dioxide is absorbed by or dissolved in the polymers, which leads to an increase in the weights of the samples; and (b) either the polymers or some agents, such as monomers, oligomers, additives, or plasticizers in the polymers are dissolved or extracted from polymer material, which leads to a decrease in the weight of the samples.¹⁶ The second mechanism can be obviously evidenced by a decrease in weight for three polymers, namely, LDPE, Nylon 66, and PP, under some experimental conditions (Table III). Other

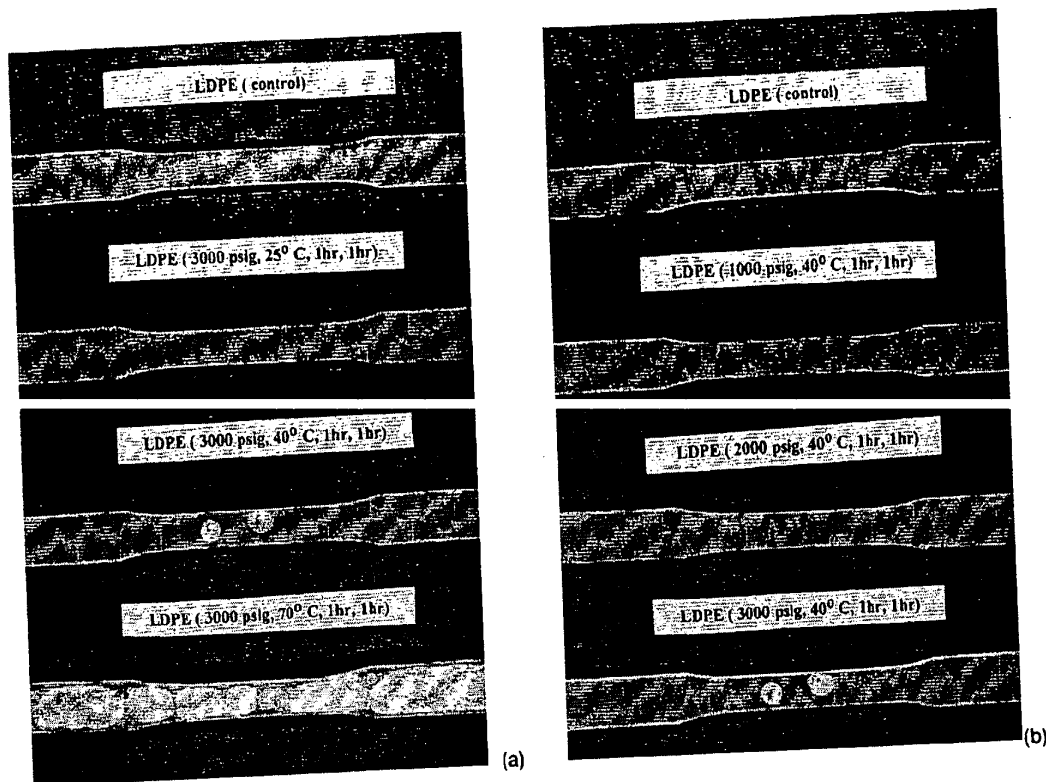


Figure 3 Photographs of the treated and untreated LDPE polymer samples.

observed changes such as the loss of precise or well-defined edges may also contribute to a loss in weight and indicate that such solubilization is also occurring. Because both dissolution of carbon dioxide into the polymer as well as polymer into carbon dioxide simultaneously occur, their effect cannot be clearly classified from the change in weight data. These effects often occur simultaneously and, in essence, are in competition during treatment; the extent of the effects varies, depending on the materials and employed treatment conditions.

Effect of the Treatment Conditions on the Weight Changes of Polymers

The effect of treatment pressures and temperatures on the observed weight changes of polymeric materials can be ascertained from the data noted in Table III. Because many changes are occurring simultaneously that will affect the observed changes, we could not correlate any direct or simple relationships between the observed weight changes and the treatment conditions employed. When the pressure

is increased, both the density and solubility parameter of the carbon dioxide do not change linearly. In addition, pressure changes can also be expected to directly affect the polymer morphology, although probably not to a very significant extent at such low pressures as employed in these experiments. Although the two mechanisms described earlier determined the resulting weight changes, one should not forget that there are many additional factors, such as structures, morphologies, values of T_g and T_m of materials, may also affect variations in the data.

Effect of the Dimensions of Samples on the Weight Changes of Polymers

Polymer samples with two different thicknesses were treated with SC CO₂ to determine the effect of dimensions on weight changes, as shown in Table III. In general, when the thickness of the sample is increasing, we found the observed weight change is increasing, with the exception of POM. It is normally expected that the polymer properties change

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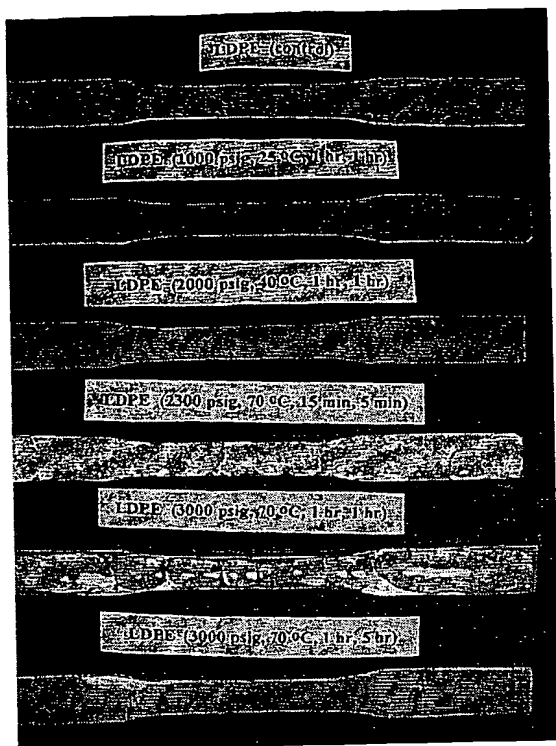


Figure 4 Photographs of the treated and untreated LDPE polymer samples showing the effect of decompression time.

in consistent with the variation in their thicknesses. Based on the same logic, CO₂ uptake should vary accordingly to the sample size based upon the surface area/volume ratio if physical properties of the polymer remain the same. But, no general relationship to cover all the polymer samples could be derived between the dimensions of samples and weight change data. The effects of cooling and annealing process of polymer manufacturing may also play a role in the polymer morphology and, in turn, the morphology of thick and thin polymer sheets may be different. A more detailed study involving polymer sheets of varying thicknesses manufactured through similar processing technique will throw more light.

Desorption of Carbon Dioxide

The absorption/dissolution of carbon dioxide in polymers was indirectly indicated by the weight change of polymers after treatment, and generally this change in mass with time showed a linear de-

pendence on the logarithm of time. The desorption (loss in weight) of CO₂ from the treated samples was notably significant immediately after removal from the treatment chamber, and the rate slows exponentially with time. Non-Fickian behavior was exhibited by the samples, indicated by the nonlinearity in the weight change data as a function of the square root of time ($t^{1/2}$) (not shown here). In Figure 5, we have plotted the weight changes for poly(vinylidene fluoride) as a function of evaluation time for the samples treated under three different conditions. In general, the weight change shows a similar trend for all the different treated samples. The samples that were treated with high pressure CO₂ showed a greater weight change than the others and the observed trend is: 3000 psi > 2000 psi > 1000 psi.

Solubility of Polymers in Carbon Dioxide

We have evaluated the solubility of polymers in carbon dioxide by gravimetry as explained earlier, at two different time periods: (1) on the same day, and (2) 8 months after treatment. The measurement after 8 months allowed a maximum desorption of dissolved carbon dioxide. Among the investigated polymers, nylon 66 showed a significant effect. As discussed earlier, changes in the weights of the polymer may be caused by dissolution/extraction⁵ of either monomers, oligomers, polymers, additives, stabilizers, plasticizers, etc.

Table IV shows a comparison between the total solubility of CO₂ in polymers and the one-dimensional solubility parameter for polymers. Though the method of treatment does not influence the solubility of CO₂, the nature of the polymer seems to play an important role, as evidenced by the solubility values. In PVDF, for example, it has been noted that a significant amount of CO₂ was dissolved in the polymer, which is likely the result of the compatibility between CO₂ and fluorine-containing compounds. An earlier report²³ involving the synthesis of high molecular weight fluorinated polymers in supercritical CO₂ confirms this observation.

At this point, it is necessary to show the relationship between pressure and density for CO₂ at 37°C (Fig. 6). It is clear from Figure 6 that there is no linear relationship between pressure and density at this temperature. Therefore, care needs to be exercised while doing experiments in this regime because of the possibility of large changes in density. Because a chosen experimental pressure strongly influences the density of the gas, the range of experimental pressure has been carefully chosen in our

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Table III Observed Weight Changes for Polymers Treated with Carbon Dioxide at Different Temperatures and Pressures

Polymer	Thickness (mm)	Weight Change (%)				
		1000 psi 40°C	2000 psi 40°C	3000 psi		
				25°C	40°C	70°C
HDPE	0.80	0.21	0.10	0.28	0.12	0.27
	2.25	0.57	0.38	0.65	1.22	—
HMWPE	3.02	0.34	0.55	0.26	0.67	1.24
	0.75	0.31	0.15	-0.02	-0.14	0.81
LDPE	2.20	1.19	0.23	1.40	1.36	—
	0.80	0.10	-0.04	-0.29	-1.14	-0.47
Nylon 66	0.60	0.05	-0.04	0.01	0.00	—
	3.20	0.89	0.69	0.79	1.81	2.02
PET	0.26	1.38	1.06	1.79	1.54	0.29
POM	0.80	0.95	1.17	1.68	2.07	—
	1.50	0.42	0.00	0.28	-0.11	0.19
PP	0.70	1.56	0.69	1.84	1.98	—
	2.25	1.00	2.73	1.15	3.02	3.58
PVDF	1.50	0.11	0.05	0.09	0.07	-0.01
	0.80	0.58	0.03	0.82	0.51	—
Teflon	1.70	—	—	—	—	—

Treatment time and decompression time were fixed as 1 h each.

investigation among 1000 and 3000 psi to cover a large change in the density of CO₂.

Influence on the Thermal Properties

Plasticization is an important phenomenon in polymer processing. The effect of plasticization will cause a marked reduction in the glass transition temperature. By treating the polymers with high-pressure CO₂, the polymers become plasticized, and such

plasticization may induce or increase crystallization during the outgas process of absorbed gases for those polymers that have the structural regularity.^{10,17}

We have chosen poly(ethylene terephthalate) (PET) as a representative polymer to investigate the effect of plasticization on crystalline polymers. Mylar sheets of 0.26 mm thickness from Du Pont were used for the investigation. As done earlier, coupon-shaped samples of 1 × 4 cm were subjected to CO₂ treatment at 3000 psi and 25°C. The time

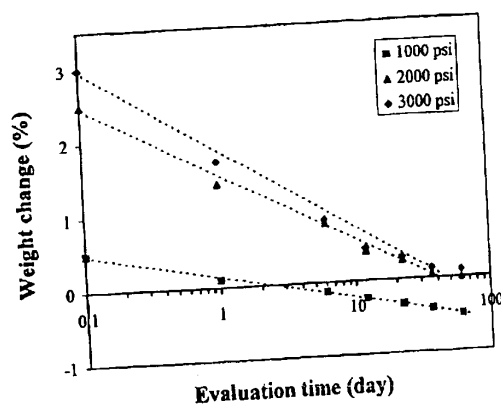


Figure 5 Changes in weight for polyvinylidene fluoride as a function of evaluation time at 40°C. Treatment and decompression time = 1 h each.

Table IV Total Solubility of Carbon Dioxide in Polymers

Polymer	Solubility Parameter	Solubility of CO ₂ (wt %)			
		C1	C2	C3	C4
HDPE	8.3	0.1	0.1	0.0	0.1
HMWPE	8.3	—	—	1.3	—
LDPE	8.3	0.0	0.2	0.4	0.5
Nylon 66	13.7	1.8	1.8	1.3	1.1
PET	10.6	—	—	1.5	—
POM	10.5	1.0	1.3	0.5	0.9
PP	8.1	0.1	0.2	0.1	0.1
Teflon	6.4	0.0	0.1	0.0	0.0

Determined gravimetrically 8 months after treatment for all the polymers except HMWPE and PET, for which the evaluation time was 5 months.

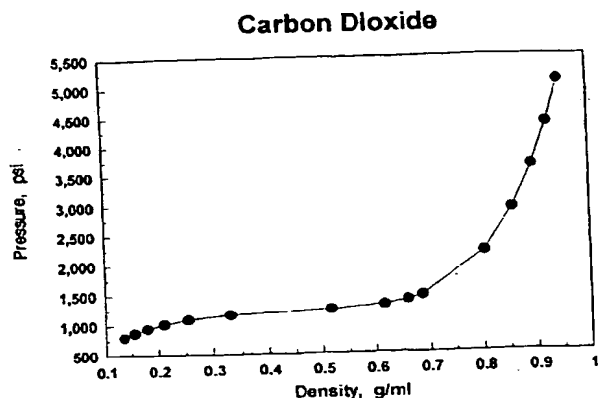


Figure 6 Pressure vs. density at 37°C for pure carbon dioxide.

for treatment and decompression was also set for 1 h each, and the treated samples were subjected to DSC and TGA evaluations at four different time intervals: (a) same day, (b) 1 day, (c) seventh day, and (d) sixteenth day. The TGA traces for PET are presented in Figure 7, and the observed results are presented in Table V, from which it is easy to understand that the amount of dissolved carbon dioxide diminishes with time continuously.

A significant increase in the degree of crystallinity for PET was noted 16 days after the treatment, which first evident on the seventh day. If absorbed by polymers, carbon dioxide is believed to be absorbed only in the amorphous regions of the material and not in the crystalline regions. Our experiments with amorphous polymers such as PMMA and PETG also confirmed this observation.²² Immediately following the treatment, the absorbed CO₂ plasticizes the amorphous regions of PET. The plasticized PET chain segments may now adopt a crystalline form because of the increased chain mobility afforded by the CO₂ solvent. The delayed observation of crystallinity can be explained by the

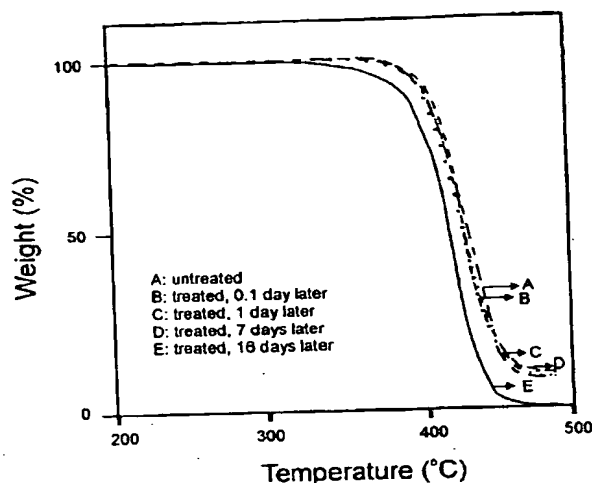


Figure 7 TGA traces for PET as a function of evaluation time. The treatment condition was CO₂ at 3000 psi and 25°C. Treatment and decompression time = 1 h each.

fact that sufficient "solvent" must diffuse out of the polymer to allow the nucleation and crystallization of the polymer chains. Hence, the degree of crystallinity was found to increase as a function of evaluation time (see Table V). The phenomenon of plasticization may be quite important in certain applications, such as the formation of polymer foams, the impregnation of polymers with chemical additives, and the separation of gas mixtures using polymer membranes and so on, as discussed earlier. These data indicate that many materials and treatment conditions can be used for applications such as cleaning, but also suggest that adverse interactions may occur in some circumstances.

Influence on the Mechanical Properties

Tensile property is also one of the most important indications of the strength of a material. We have

Table V Thermogravimetric Data Showing the Amount of Carbon Dioxide Uptake, Crystalline Melting Temperature, and Enthalpy for PET

Evaluation Time (Days)	Weight Loss at 170°C (%)	CO ₂ Uptake (%)	T _m (°C)	ΔH (cal/g)
Untreated	-0.36	—	259	6.5
0.1	-1.08	0.72	—	—
1.0	-0.67	0.31	—	—
7.0	-0.52	0.16	261	6.9
16.0	-0.50	0.14	262	9.5

Treated in carbon dioxide at 3000 psi and 25°C for 1 h.

tested the (1) yield strength (tensile strength at yield), (2) ultimate elongation (elongation at break), and (3) modulus of elasticity for five different crystalline polymers namely: PP, POM, Nylon 66, LDPE, and HDPE.

The dumbbell-shaped test specimens conforming to the dimensions of Type I in ASTM D638 were prepared from plastic sheets by cutting them using a guide mold. A universal testing machine (an Instron Model 6025) was used for the stress-strain measurements. The testing machine had a fixed and a movable grip on the top and bottom, respectively. The distance between two grips was 11.43 cm, and the rate of motion of the driven grip was controlled at 5.1 cm/min. The testing was performed at $23 \pm 2^\circ\text{C}$. As mentioned earlier, five specimens were used for each sample in the testing. Samples treated with SC CO_2 were evaluated 30 days after treatment, to allow for the complete loss of CO_2 from the polymers. The yield strength, ultimate elongation, and modulus of elasticity were obtained from the stress-strain curves involving standard procedures (Table VI).

For the materials studied, the yield strength varies in a broad range from 10.7 MPa for low-density polyethylene (LDPE) to 73.7 MPa for Polyoxymethylene (POM). LDPE has high flexibility and a low degree of crystallinity and so, when a stress is applied, the polymer chains readily disentangle or slip. As a result, LDPE shows high ultimate elongation and low modulus. On the other hand, POM has a very high degree of crystallinity, which can restrict disentanglement or slippage among polymer chains when a stress is applied.

In general, the increase in yield strength and modulus and the decrease in ultimate elongation suggested that the degree of crystallinity had been increased during the SC CO_2 treatment. Weight change data is not much related to plasticization because polymers such as HDPE, LDPE, and PP show almost no change in their weight after treatment; however, these polymers do show the occurrence of plasticization based on decreases in their modulus of elasticity and yield strength. There is no evidence that high-pressure carbon

Table VI Effect of SC CO_2 Treatment on the Mechanical Properties of the Crystalline Polymers

Polymer	SCF Treatment Condition	Yield Strength (MPa)	Ultimate Elongation (%)	Modulus of Elasticity (MPa)
PP	Control	36.2	> 300	1370.3
	C1	36.5	> 300	1408.3
	C3	35.5	> 300	1297.9
	C6	35.0	> 300	1248.3
	C7	34.5	178	1172.4
	Control	73.7	11	2595.2
	C1	73.7	10	2489.6
POM	C3	73.6	11	2493.1
	C6	73.7	9	2454.5
	C7	72.9	10	2391.7
	Control	68.5	48	2003.4
	C1	72.2	30	2063.4
	C3	73.3	24	2055.8
	C6	74.1	25	2063.4
Nylon 66	C7	74.7	22	2185.5
	Control	10.7	238	420.7
	C1	11.2	270	383.4
	C3	10.9	224	377.9
	C6	10.6	75	341.4
	C7	10.2	223	397.2
	Control	26.4	92	1116.5
LDPE	C1	26.9	87	1108.3
	C3	26.6	92	1064.8
	C6	26.8	97	1073.8
	C7	26.3	161	1037.2
	Control	26.4	92	1108.3
	C1	26.9	87	1064.8
	C3	26.6	97	1073.8
HDPE	C6	26.8	97	1073.8
	C7	26.3	161	1037.2

C: control; C1: 1000 psi, 25°C , 1 h; C3: 2000 psi, 40°C , 1 h; C6: 3000 psi, 70°C , 1 h; and C7: 3000 psi, 70°C , 1 h, 5 h.

dioxide can destroy the crystallites within these polymers.

CONCLUSIONS

The systematic study on the interaction of carbon dioxide with nine different crystalline polymers has been performed, and various influencing parameters such as effect of pressure and temperature were studied. From the simple gravimetric procedure, we can get the solubility of CO₂ into various polymers. From the observed results, one can conclude that a SCF treatment can be tailored to have either no effect or detrimental effect for the needed applications, by adjusting the treatment or decompression time, pressure, and/or temperature, and other influencing parameters, for the needed applications. The interaction of CO₂ with a series of 11 different amorphous polymers has also been investigated,²² and the changes in weight, thermal, and mechanical properties were followed. It has been found that they can absorb carbon dioxide in a greater extent than crystalline polymers and, in turn, the phenomenon of plasticization was also very high.

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